

Note

On Crystallization of Comblike Polymethacrylates

Most investigators who studied the crystallization and melting of comblike polyacrylates and polymethacrylates observed only a single melting point for these materials and reported no evidence for polymorphism related to side chain crystallinity.¹⁻⁴ Sobottka and Sochava, however, who examined the melting behavior of atactic poly(hexadecyl acrylate) and poly(octadecyl methacrylate) using differential scanning calorimetry (DSC), reported two melting endotherms for both materials and ascribed them to two distinct crystalline forms.⁵ When they annealed the polymers in the vicinity of the melting points, the amount of higher melting polymer grew with time at the expense of the lower melting one. This was interpreted as being analogous to the polymorphism observed by Turner-Jones in hydrocarbon polymers with side chain crystallinity.⁶

We wanted to resolve these ambiguities regarding polymethacrylates since these materials are widely used as pour point depressants for lubricating oils and their effectiveness is related to crystallization and melting behavior.^{7,8} We have, therefore, examined in some detail the crystallization of poly(octadecyl methacrylate) and a copolymer of octadecyl methacrylate and hexadecyl methacrylate. While we were able to identify two distinct melting endotherms in these materials as described by Sobottka and Sochava, we believe that they exist in just a single crystalline modification and the two melting points are the result of different crystallization processes.

EXPERIMENTAL

Octadecyl methacrylate was prepared in toluene by direct esterification of methacrylic acid with 1-octadecanol using methanesulfonic acid as catalyst and trace amounts of MEHQ to inhibit polymerization. The product was purified by several recrystallizations from methanol. Its melting point was 29.5–30.2°C and its IR spectrum corresponded to that of the desired product. Purity, by GC analysis, was 98%. Polymerization of the octadecyl methacrylate was carried out in cyclohexane at reflux using azobisisobutyronitrile as the catalyst. The polymer was precipitated into methanol and then washed several times with hot methanol and acetone. Analysis by pyrolytic GC showed 99% poly(octadecyl methacrylate). Molecular weights were obtained by GPC; \bar{M}_w and \bar{M}_n were, respectively, 287,000 and 132,000.

The copolymer of octadecyl methacrylate and hexadecyl methacrylate was a commercial material from Scientific Polymer Products, Inc. sold as a concentrate in toluene (Cat. #167C). It was precipitated by methanol and purified as described above. Pyrolytic GC gave 62.0% octadecyl, 32.0% hexadecyl, and 3.6% tetradecyl methacrylates as its major components. GPC results on samples from two batches were, respectively, 142,000–147,000 for \bar{M}_w and 45,000–54,000 for \bar{M}_n .

Samples for crystallization studies were heated at 60°C for 20 min to remove any traces of residual crystallinity. This was followed by quick transfer to a constant temperature bath for isothermal crystallization at the desired temperature. To obtain the DSC runs, we employed a DuPont 990 thermal analyzer at a scanning rate of 10°C/min on samples of 5–10 mg. A Scintag Pad V system was used for the powder diffraction diagrams. To avoid melting of polymers during the runs, when necessary we precooled the samples before they were placed in the X-ray beam.

RESULTS AND DISCUSSION

In almost all cases, DSC scans of poly(octadecyl methacrylate) consisted of one well-defined peak consistent with a single crystalline structure. The location of the peak varied appreciably with sample treatment. Quenching molten polymer in a dry ice–acetone mixture gave a peak at about 35–36°C; slow cooling from 60°C to room temperature over 2 h resulted in a peak at 40–42°C.

Melting polymer samples at 60°C was followed directly by aging at selected temperatures. Aging at 28°C at up to 42 h invariably gave single DSC peaks. The major change observed with

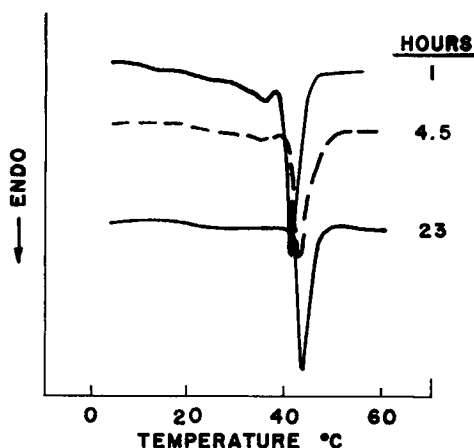


Fig. 1. Effect of isothermal crystallization at 32.8°C on DSC scans of poly(octadecyl methacrylate).

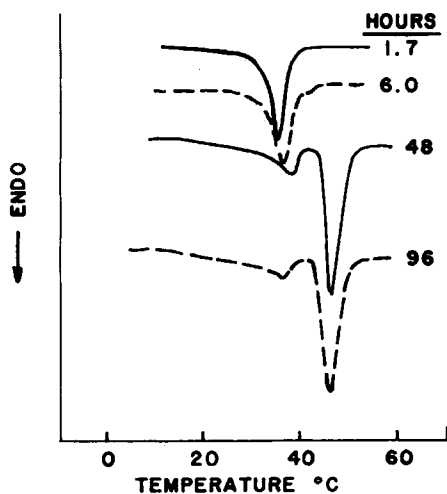


Fig. 2. Effect of isothermal crystallization at 35°C on DSC scans of poly(octadecyl methacrylate).

time was a gradual increase in the area under the peaks accompanied by narrowing of the peaks and a shift from 36.5 to 42°C, all consistent with an increase in crystallinity and decrease in crystalline defects. The situation on aging the samples at 32.8°C is depicted in Figure 1. After 1 h we observe a small peak at 36°C and a large one at 42°C. As the polymer is aged further, the lower peak is replaced by a shallow depression, indicating the presence of small amount of material with a melting range of about 20–36°C. Results on aging at 35°C are shown in Figure 2. They differ appreciably from those above. The large concentration of lower melting crystals gradually gives way to the higher melting ones, and at 48 h these form the predominant species. There is no further change on doubling the aging time to 96 h.

X-ray diffraction patterns of both high- and low-melting versions of poly(octadecyl methacrylate) are shown in Figure 3. As seen, the 2θ values are the same for both. IR spectra of both polymer versions were identical in every respect and in agreement with the published spectrum.¹ The presence of a singlet in the vicinity of 720 cm^{-1} , rather than a doublet, was consistent with a hexagonal structure.

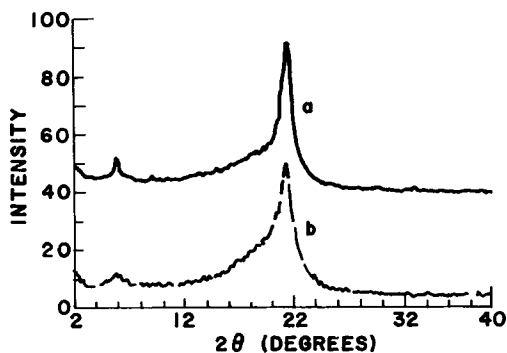


Fig. 3. X-ray diffraction diagrams of poly(octadecyl methacrylate): (a) slowly crystallized with mp at 42°C; (b) shock-cooled with mp at 36°C.

Sobotka and Sochava⁵ ascribed the two DSC peaks to different crystalline species and the gradual disappearance of one and growth of the other, in their case at 33.5°C, to transformation of a crystalline structure involving the side groups only to one in which the main chains also participate in the formation of the crystallites. Our data showed no evidence for polymorphism and thus are incompatible with this interpretation. A different interpretation has to be sought, therefore, for the double melting peaks. It is reasonable to postulate that quenching leads to extremely rapid nucleation and crystallization, resulting in many small crystals of poor quality with a low melting point. The broader X-ray diffraction peaks and more pronounced amorphous halo of the quenched sample in comparison with that of the high melting polymer support this view. At 35°C, crystallization is very slow and leads to well-formed, large crystals with high melting points. Removal from the bath before the process is complete produces rapid crystallization from the residual amorphous phase, resulting in two melting endotherms on DSC scans. Large amounts of the higher melting crystals in the sample severely restrict mobility in the amorphous phase, giving rise to extremely poor crystals with the broad melting range seen in some of the DSC scans. At 32.8°C, the crystallization is fast enough so that very little of the lower melting form is seen, even after only 1 h.

The results on the copolymer, which was examined in less detail than the poly(octadecyl methacrylate), were generally similar to those on the latter. Single DSC endotherms were obtained on both quenching and slow cooling. Two peaks were observed on isothermal crystallization at 27°C. The lower peak appeared at 27–32°C and the higher between 36 and 40°C. Typical X-ray diagrams are shown in Figure 4. Both shock-cooled and slowly crystallized samples have the same crystalline peaks; they differ primarily in the amount of amorphous material present. As in the homopolymer, irrespective of melting point, only one crystalline structure was present. The

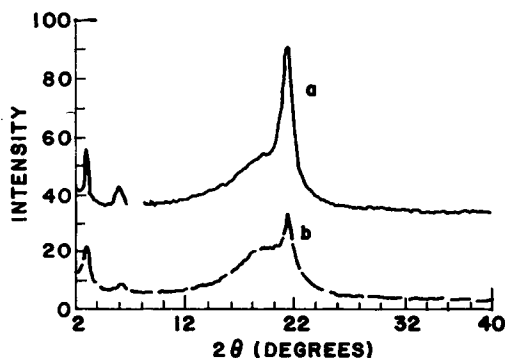


Fig. 4. X-ray diffraction diagrams of copolymer of octadecyl and hexadecyl methacrylates: (a) slowly crystallized with mp at 38°C; (b) shock-cooled with mp at 32°C.

results are thus consistent with isomorphous replacements in polymethacrylate copolymers with side chains of different lengths.⁴

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References

1. K. Yokota, T. Koguo, and T. Hirabayashi, *Polym. J. (Tokyo)*, **15**, 891 (1983).
2. Y. Shibasaki and K. Fukuda, *J. Polym. Sci., Polym. Chem. Ed.*, **18**, 2437 (1980).
3. E. F. Jordan, Jr., D. W. Feldeisen, and A. N. Wrigley, *J. Polym. Sci., A-1*, **9**, 1835 (1971).
4. S. A. Greenberg and T. Alfrey, *J. Am. Chem. Soc.*, **76**, 6280 (1954).
5. I. Sobottka and I. V. Sochava, *Vysokomol. Soyed.*, **A21**, 1322 (1979).
6. A. Turner-Jones, *Makromol. Chem.*, **71**, 1 (1964).
7. L. E. Lorensen and W. A. Hewett, Am. Chem. Soc. Meet., Sep. 9-14, 1962, Petrol. Div. Preprint 7 (4B), pp. B71-85.
8. E. F. Jordan, Jr., S. Smith, Jr., R. D. Zabarsky, and A. N. Wrigley, *J. Appl. Polym. Sci.*, **22**, 1547 (1978).

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